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Stereoselective PCO/POC-Rearrangement of P-C-Cage Phosphorane in the Reaction of 4,5-Dimethyl-2-(2-oxo-1,2-diphenyl)ethoxy-1,3,2-dioxaphospholane with Hexafluoroacetone

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Abstract

© 2016 American Chemical Society.Interaction of 4,5-dimethyl-2-(2-oxo-1,2-diphenyl)-thoxy-1,3,2-dioxaphospholane, bearing a carboxyl group in the γ-position with respect to the phosphorus atom and obtained from d,l-butanediol, with hexafluoroacetone (CCl4, -40 °C) leads to the simultaneous formation of regio- and stereoisomeric cage-like phosphoranes with phosphorus-carbon and phosphorus-oxygen bonds with a high stereoselectivity (>95%), whose structure was determined by 1D and 2D NMR spectroscopy and XRD. When stored as a solution in dichloromethane for one month, the PCO-isomer rearranges into the thermodynamically more stable POC-isomer of the cage-like phosphorane. Mild hydrolysis of the PCO/POC-isomers proceeds with a high chemoselectivity and leads to the formation of P(IV)-dioxaphospholane derivatives. Acidic hydrolysis of the POC-isomer leads to the formation of an oxirane derivative with an unexpectedly high stereoselectivity (>95%). DFT calculations (using the PBE functional) allowed us to obtain structures and energies of the initial phospholane, reaction products (PCO/POC-isomers), and an intermediate P(V)-oxaphosphirane.

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